Photochemical Transformations of the Structural and Optical Properties of Marine Colored Dissolved Organic Material in Coastal Waters

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LONG-TERM GOALS

My long term goals are to develop an understanding of the photochemical processes affecting CDOM, and the resultant changes in its optical properties and molecular composition, particularly in coastal environments.

OBJECTIVES

My objectives were to: 1) complete and publish on-going studies applying field flow fractionation to the characterization of CDOM in fresh to marine transition zones in South Florida (with Rod Zika (RSMAS, UM)); 2) set up instrumentation and accumulate water samples from a range of fresh vs. marine sites for photochemical experiments in my new laboratory; and 3) organize and cochair a special session on results from recent ONR-funded cruises at the 2002 Ocean Sciences meeting.

APPROACH

In collaboration with Dr. Rod Zika and Eliete Zanardi-Lamardo (graduate student) at RSMAS, our approach to CDOM characterization is to use Flow Field Flow Fractionation (FFFF) as the separation technique, together with optical characterization of fractionated CDOM by in-line absorbance and fluorescence. These studies will be extended to structural characterization by ion trap mass spectrometry (LC/MS^n) with Erik Stabenau (graduate student). Over the last year, FFFF studies on a series of riverine and marine DOM samples from South Florida waters were completed, along with photochemical studies to see if irradiation of fresh CDOM produces material with the same structural and optical characteristics as marine CDOM. Photochemical experiments are performed with a laser for pulsed single wavelength irradiations and a xenon lamp for continuous multi-wavelength irradiations. Gulf of Mexico coastal water samples were collected for this laboratory in collaboration with Dr. Bob Chen, U. Mass. Boston and Rod Zika, RSMAS. Field studies and sampling of local salt marshes and coastal waters were carried out within a larger on-going research project led by Dr. Stanley Grant (UCI), with Dr. Jim Noblet (Southern California Coastal Water Research Project) and Dr. Charlie McGee and Dr. Sam Mowbray (Orange County Sanitation District).

WORK COMPLETED

Over the last year, initial FFFF studies on CDOM in two South Florida fresh to marine transition zones were completed. This technique has been previously used to characterize soil and riverine humic substances, but this is its first application to CDOM in such systems. Size separation in FFFF relies on

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14. ABSTRACT
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15. SUBJECT TERMS

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the molecular diffusion coefficient i.e. molecular size, and offers some advantages compared to other common DOM fractionation techniques that suffer from charge adsorption and charge repulsive effects. Eliete Zanardi-Lamardo, a fifth-year PhD. student, is working on the FFFF analysis of CDOM in coastal waters for her dissertation research. Over the last year, FFFF was applied to DOM samples from the Shark and Caloosahatchee Rivers in Southwest Florida. Optimal operating parameters for DOM fractionation were determined using humic standard materials and natural samples. The FFFF system was calibrated with commercial polystyrene standards of known molecular sizes. Frit inlet/frit outlet (FIFO) was coupled to FFFF to concentrate samples inside the channel and improve stability, reproducibility and sensitivity. Following separation, the absorbance and fluorescence of the size-fractionated components in the FFFF eluent were detected with in-line diode array UV-VIS (200 – 700 nm) and fluorescence detectors. One manuscript has been published on the methodology for CDOM in natural waters, and one has been submitted on the differences in CDOM between the two rivers and fresh to marine waters.

A photochemical system has been set up in my new laboratory, incorporating a nitrogen laser and xenon lamp for irradiations and associated optics and electronics for data acquisition. One manuscript on previous lifetime measurements of CDOM using a nitrogen laser is in press (in collaboration with Dr. Gil Jones (Boston University) and Dr. Rod Zika and Eliete Zanardi-Lamardo (RSMAS))

A library of coastal water samples is been accumulated in this laboratory for future optical and structural studies. Samples were collected and exchanged on two cruises in the coastal waters of the Gulf of Mexico. In April, 2001, Bob Chen took samples in the Mississipi River. In September 2001, Cindy Moore took samples for us on a cruise from RSMAS up the west coast of Florida, revisiting the sites from last year's large ONR-funded multi investigator cruise in June 2000. I had hoped to participate in this cruise with a student, but cruise dates were unfortunately pushed back into the start of classes in the Fall semester. Samples will also be taken for this laboratory on the second upcoming November cruise from RSMAS.

Local coastal and salt marsh water samples have also been taken. In June/July 2001, I participated in a large study of the waters of two salt marsh systems (Newport and Oxbow Sloughs) that drain into the surf zone at Huntington Beach, and may impact beach quality in this area. Huntington Beach is frequently closed due to high bacterial counts, which may originate in the marshes from birds or anthropogenic inputs i.e. sewage leaks. Over three weeks, water samples were taken for six tidal cycles at the entry/exit points into the sloughs. My interest was in any potential differences between CDOM in the incoming tides (coastal seawater) vs. the outgoing tides (saltmarsh water) due to different sources. The salinity, absorbance and 3D fluorescence of these samples were measured. This study was conducted in the low flow dry season. We will return to this site for a second 3-week study in January, the wet season, and expect significantly higher freshwater inputs then.

A special session titled "CDOM in the Coastal Ocean: Transformation Processes and Their Effects on Optical Properties" was proposed and accepted for the upcoming National Ocean Sciences meeting (February 2002, Honolulu). My co-conveners are Dr. Paula Coble (USF) and Dr. Rod Zika (RSMAS). This session will serve as a focused venue for results from the many ONR-funded cruises and studies over the last few years that have addressed these questions. An announcement will shortly be sent to all ONR PIs in the Biological and Chemical Oceanography Division and other potential presenters in this area.

RESULTS

FFFF was used to characterize CDOM samples from two Southwest Florida rivers (Caloosahatchee (CR) and Shark (SR)). The SR receives DOM from the Everglades and discharges into Florida Bay. By contrast, the CR drains Lake Okeechobee in central Florida, receiving anthropogenic inputs and farming run-off. Two different molecular mass (MM) distributions of CDOM in low salinity water samples from both rivers were identified by fluorescence: one centered at ~1.7 kDa (CR) and ~2 kDa (SR); the second centered at ~13 kDa for both rivers. The higher MM fluorescent fraction disappeared gradually in the river plumes to below detection limit in coastal waters. Only one MM distribution centered at ~2 kDa (CR) and 2.2 - 2.4 - kDa (SR) was detected by absorbance. Fluorescence in general peaked at a lower MM than absorbance, suggesting a different size distribution for fluorophores vs. chromophores. One interesting feature for the Shark River is that the peak maximum of the lower absorbance MM fraction decreased 12% (2.40 to 2.12 kDa) with increasing salinity, giving a lower MM distribution in more saline waters (Figure 1). A photochemical study showed that fresh waters irradiated by sunlight have similar characteristics to more marine waters, including a shift in the MM distribution of chromophores to lower values. The differences observed between the rivers in the optical characteristics, MM distributions and diffusion coefficients suggested that the CDOM inputs, mixing rates, and photochemical degradation processes are different for these two rivers.

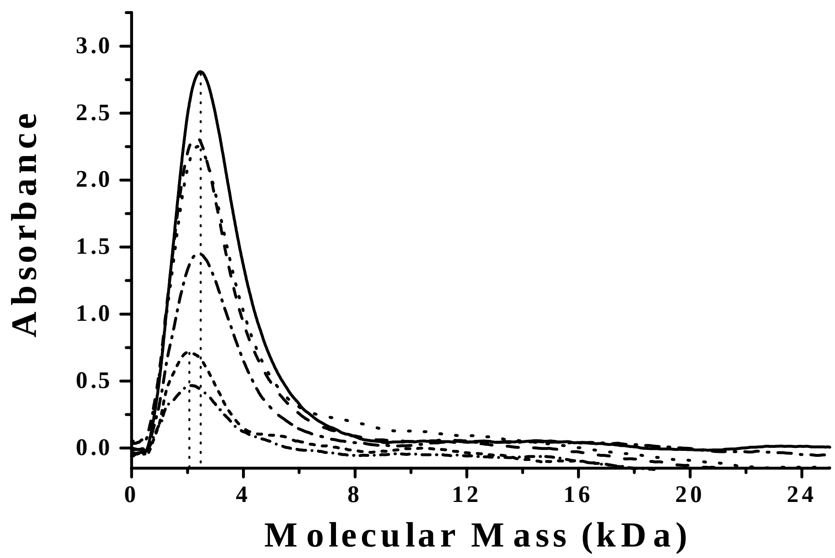

Figure 1: Absorbance (330nm) as a function of molecular mass (kDa) for a fresh to more marine transition zone in the Shark River.
[Absorbance peaks at a molecular mass of ~2.4 kDaltons, but as the salinity increases the absorbance decreases and the peak maximum shifts to lower molecular masses]

Preliminary studies were also undertaken in a local coastal water system, a Southern Californian salt marsh (June 26th - July 21st). For six tidal cycles, samples were taken from the exits of the Newport and Oxbow Sloughs at the flood control gates at the peak of the flood tide, just after the flood tide, and at the lowest point of the ebb tide. The Newport Slough is considered a control slough with a native bird population. The Oxbow Slough is an anthropogenically-impacted slough, with an oil refinery, trailer park and a duck feeding station. The hypothesis was that salt marshes are a source of CDOM and bacteria. On ebb tides, the water flows from the sloughs into the surf zone and should have higher absorbance. Conversely, during the flood tide, seawater flows into the sloughs, and samples should have lower absorbance.

Salinity was fairly constant at 31-33 and the pH ranged from 7.3 and 7.85. In general, lower pH values occurred at low tides when water flow was coming out of the sloughs. For an ebb tide, absorbances were about two to three times higher than absorbances for the incoming flood tides as expected. In general, all absorbance spectra showed a simple exponential fall off in intensity with increasing wavelength, typical of natural waters containing CDOM. Several samples showed unusual behavior with lower or higher slopes, shoulders or peaks. These occurred during a chlorophyll bloom in the coastal waters. A co-variance analysis of UV-VIS absorbance at 254 nm vs. 285 nm has been previously used to differentiate between late season and early season sources of CDOM in storm water flows in the Upper Santa Ana River watershed (Izbicki et al., 2000). This is the watershed that surrounds the sloughs. A similar analysis was applied here, and is shown in Figure 2. The excellent linearity and the fact that the data fall on a single straight line suggests no significant difference between material in the in-coming tide vs. that draining the slough. This suggests a well-mixed environment with a single source of CDOM. The exceptions are three samples that lie slightly off the line, but these correspond to the chlorophyll bloom and likely a different source. Since absorbances are consistently higher at low tide when flow is out of the sloughs with less dilution, this suggests the salt marshes are acting as the dominant source of CDOM.

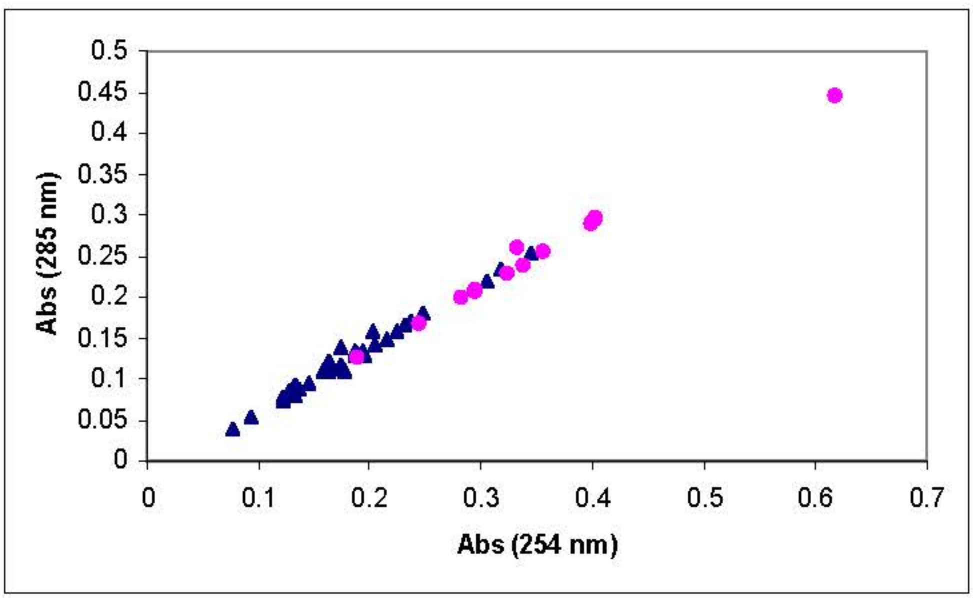

Figure 2. A linear co-variance plot of absorbance (at 285 nm) vs. absorbance (at 254 nm) for Newport and Oxbow Sloughs for low tide (circles) vs. high tide (triangles). (Uncorrected absorbances; 10 cm cell).

IMPACT/APPLICATIONS

FFFF is a novel analytical technique for CDOM that has proven useful in correlating structural changes i.e. size with changes in absorbance and fluorescence. It is appropriate to use in future investigations of the structural and associated optical features of this material. Correlating these changes in optical characteristics under the action of sunlight with associated changes in structural features will allow us to understand how ultraviolet/visible radiation is attenuated in coastal environments.

TRANSITIONS

The data collected in the sloughs in June/July 2001 are been used by Stan Grant (UCI) and Jim Noblet (SCCWRP) in their analysis of potential sources of changing bacterial levels in the water. A joint manuscript is planned.

RELATED PROJECTS

In a related ONR YI grant, I am examining the effect of quinone moieties on the photochemistry of CDOM in coastal waters. Specifically, I will be using NMR techniques for structural characterization, along with measurements of photochemical products, to correlate specific structural features with enhanced photochemical activity and determine if quinone functionalities are the key feature in CDOM that absorbs sunlight and produces transient products such as peroxide.

In continued studies of CDOM in local coastal systems in collaboration with Stan Grant (UCI), Jim Noblet (SCCWRP) and the OCSD, I will be sampling two salt marshes in January 2002. In a multi-investigator project recently funded by the NSF, I will also be incorporating GIS and field studies of the Upper Newport Back Bay, an ecological reserve, into undergraduate geoscience courses. This will provide additional opportunities for collecting different source waters.

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